Viscosity Measurements on Nitrogen

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The viscosity coefficient of gaseous nitrogen was measured with a vibrating-wire viscometer of very high precision. The measurements were performed along the six isotherms of (298.15, 323.15, 348.15, 373.15, 398.15, and 423.15) K and at pressures up to a maximum of 35 MPa. The gas densities needed for the evaluation of the measuring values were calculated using an equation of state by Span et al. (*J. Phys. Chem. Ref. Data* **2000**, *29*, 1361−1433). The reproducibility is ± 0.05 %, whereas the total uncertainty is estimated to be ± (0.2 to 0.3) %. The viscosity values of the isotherms were evaluated with a power series expansion in terms of reduced density. A comparison with the most recent correlation by Lemmon and Jacobsen (*Int. J. Thermophys.* **2004**, *25*, 21−69) shows that the new values agree in the temperature and density ranges of the measurements within ± 0.7 %. Based on a comparison with the most reliable data from the literature, it is concluded that the new values are appropriate to improve the viscosity surface correlation of nitrogen.

Introduction

Air is one of the working fluids mostly used in industrial applications, such as in combustion processes, compressors, and turbines. Unfortunately, the thermophysical properties of air have not been investigated very often and with sufficiently high accuracy. The reason for that is the risk of measurements on oxygen or on mixtures with a high content of oxygen. On the contrary, the thermophysical properties of nitrogen as the main component of air have been measured rather frequently with high accuracy. The most recent reference equation of state for the thermodynamic properties of nitrogen was reported by Span et al.[1] The uncertainty in the density using this equation is estimated to be less than ± 0.05 % in the temperature and pressure ranges of the viscosity measurements of the present paper.

The transport properties of nitrogen have not been determined with the same high accuracy as the thermodynamic data. Stephan et al.,[2] Millat and Vesovic,[3] and Lemmon and Jacobsen[4] presented transport property surface correlations for nitrogen in the complete fluid ranges. Whereas Millat and Vesovic did not give detailed information about the uncertainty of their correlation, Stephan et al. reported standard deviations for the viscosity of ± 0.3 % in the dilute-gas region and of ± 1 % for densities up to 18 mol·dm^{-3} considering only a limited number of data sets from literature. The most recent correlation by Lemmon and Jacobsen is based on an extended database resulting in comparably higher uncertainties of the viscosity: ± 0.5 % in the dilute-gas region and ± 2 % in the temperature range of (270 to 370) K up to pressures of 100 MPa as well as higher values at the extremes of the fluid range. Nevertheless, this correlation will be used as the basis for a comparison, since further and new results of viscosity measurements have been taken into account as compared with the older correlations. With regard to the development of a high standard for the test and implementation of instruments for viscosity measurements on gases, the uncertainties of the mentioned correlations are still too large and should be further improved. The new measurements of the viscosity of nitrogen are intended to provide high-precision values in the temperature range of (298 to 423) K and up to moderate pressures of 35 MPa.

Some years ago Wilhelm et al.[5] designed a vibrating-wire viscometer and performed high-precision measurements on argon, krypton, and propane[6,7] and, recently, on sulfur hexafluoride.[8] A special measuring program was arranged to determine the viscosity of natural gas components and of natural gas mixtures to fulfill the needs of the gas industry. In addition to the investigation on propane, the viscosity of methane,[9,10] of two natural gases,[10,11] and very recently of ethane[12] were determined. The measurements on nitrogen reported in this paper complement this program.

Experimental Section

A detailed description of the design and implementation of the vibrating-wire viscometer has been given by Wilhelm et al.[5] and Wilhelm and Vogel[6] so that only some essential items should be summarized here. The wire with a length of 90 mm and a diameter of about 25 μm is placed in a magnetic field in such a manner that all even and the third harmonic modes are suppressed. Chromel has been selected as wire material due to its comparably smooth surface. The oscillation is initiated by a sinusoidal voltage pulse with a frequency close to the resonant frequency of the wire. The oscillation following the pulse is detected by amplifying the induced voltage and measuring it as a function of time. One hundred oscillation curves are recorded and averaged to improve the signal-to-noise ratio. Comparably large displacements contrary to the requirements of the measuring theory are applied in order to obtain reasonably large measuring signals. Finally, the logarithmic decrement (Δ) and the frequency (ω) of the oscillation, determined for different values of the relative initial amplitude $\epsilon = y_{max}/R$ (y_{max} − initial

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10.1021/je050399c CCC: $33.50
Published on Web 01/11/2006

wire displacement, R − wire radius), are deduced by an extrapolation of $\epsilon^2 \rightarrow 0$.

The viscometer cell is suspended from the top closure of a pressure vessel placed in a heat-pipe thermostat. The pressure is determined with four transmitters supplied by Digiquartz. Their working ranges of (0.69, 2.76, 13.8, and 41.4) MPa are characterized by uncertainties of ± 0.01 % of full scale. The temperature is obtained by means of a premium ITS-90 thermometer and a $6^1/_2$ digit multimeter with an uncertainty of ± 0.015 K.

The theory of the vibrating-wire viscometer[13] provides working equations for the calculation of the viscosity (η) from the deduced values Δ and ω. For that purpose, the density (ρ) of the fluid, the density (ρ_s), and the radius (R) of the wire as well as the values Δ_0 and ω_0 in vacuo are needed. The wire radius (R) has been derived from viscosity measurements on argon at room temperature to be (12.770 ± 0.005) μm. In doing so, reference values by Kestin and Leidenfrost[14] were used assuming the density of the wire material chromel to be 8500 kg·m^{-3} as given by the supplier.

Measurements and Results

The certified purity of nitrogen supplied by Messer Griesheim (Germany) was 99.999 %. The isotherms at (298.15, 323.15, 348.15, 373.15, 398.15, and 423.15) K cover a pressure range up to 35 MPa. The densities (ρ) were calculated from the measured pressures (p) and temperatures (T) with the equation of state by Span et al.[1]

The isothermal series of measurements comprise about 50 data points apart from the 298 K isotherm. The individual points were not measured exactly at the nominal temperatures, but the deviations of the experimental temperatures were kept within ± 0.05 K for the first three isotherms and within ± 0.1 K for the higher ones. Hence, the experimental viscosity values were adjusted to the nominal temperature using a Taylor expansion restricted to a second power in temperature. In this procedure, the densities directly derived from the experiments and those for the isotherms are the same. Then the pressures at the nominal temperatures of the isotherms were recalculated from the densities. The results for all series of measurements are listed as triples of pressure, density, and viscosity in Table 1. The experimental values at pressures of about 0.1 MPa were controlled with regard to a possible influence of slip due to a comparably small density. This effect was observed in the measurements on propane,[7] sulfur hexafluoride,[8] and methane.[10] But only one value in each series of measurements was found to be influenced by slip. These values are included, but marked in the table, and excluded from further evaluation.

The reproducibility of the measurements is better than ± 0.05 %. With regard to the absolute uncertainty, errors resulting from the calibration values by Kestin and Leidenfrost,[14] which are characterized by an uncertainty of ± 0.1 %, as well as from the density determination have to be considered above all. In general, an uncertainty of ± 0.05 % of the density data contributes a change of ± 0.025 % in the viscosity, whereas the allocation error related to temperature and pressure is not exceeding ± 0.02 %. As a result, the total uncertainty of the viscosity values is estimated to be about ± 0.2 %, possibly increasing up to ± 0.3 % at the highest measured pressures.

Analysis

The experimental results of the isotherms were correlated as a function of the reduced density (δ) by means of a power series representation restricted to the fourth or a lower power depending on the included density range.

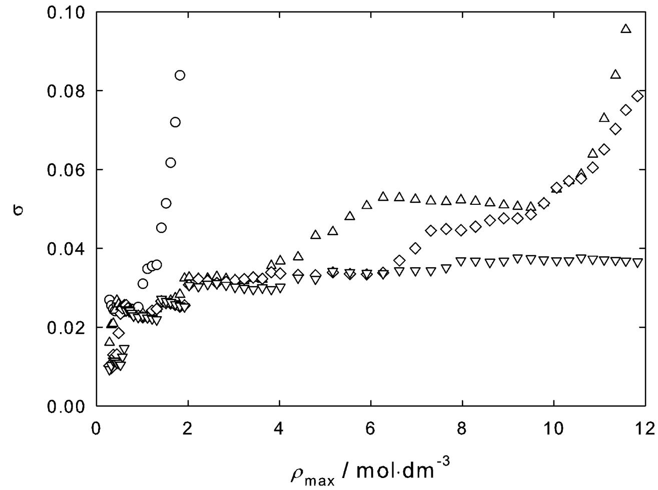

Figure 1. Evaluation of the 298.15 K isotherm with a power series expansion in the reduced density (δ) (eq 1). Representation of the weighted standard deviation (σ) as a function of the maximum molar density (ρ_{max}) for which experimental points are included. ○, first order in δ; △, second order in δ; ◇, third order in δ; ▽, fourth order in δ.

$$\eta(\tau, \delta) = \sum_{i=0}^{n} \eta_i(\tau)\delta^i \tag{1}$$

$$\delta = \frac{\rho}{\rho_{c,N_2}} \quad \rho_{c,N_2} = 11.184\ \text{mol·dm}^{-3}$$

$$\tau = \frac{T}{T_{c,N_2}} \quad T_{c,N_2} = 126.192\ \text{K}$$

The values of the critical constants correspond to that given by Span et al.[1] Weighting factors of $(100/\eta)^2$ were used in the multiple linear least-squares regression to minimize the relative deviations. The weighted standard deviation (σ), related to the maximum density of the experimental points included in the fit by means of eq 1, was used as criterion for the description of the considered isotherm.

Figure 1 shows that for the 298.15 K isotherm, which includes experimental values up to 11.8 mol·dm^{-3}, a series expansion according to eq 1 with a fourth order in the reduced density (δ) is needed. For the higher isotherms a series expansion of either fourth or third or even second power is appropriate to describe the experimental points. The power in δ of the series expansion needed for all six isotherms and the values of the coefficients (η_i) are given in Table 2. Table 2 shows that the density coefficients (η_1 to η_4) seem to be only weakly temperature dependent.

With respect to a comparison with data from the literature discussed below, the experimental data of all isotherms were correlated with a double polynomial series expansion according to the following equation for which the coefficients η_{ij} are given in Table 3:

$$\eta(\tau, \delta) = \sum_{i=0}^{4} \sum_{j=0}^{2} \eta_{ij} \frac{\delta^i}{\tau^j} \tag{2}$$

Figure 2 illustrates that the deviations of the experimental values from the fit are practically within ± 0.1 for all isotherms. This

Table 1. Experimental Viscosity Values of Nitrogen along Isotherms

p / MPa	ρ / mol·dm^{-3}	η / μPa·s	p / MPa	ρ / mol·dm^{-3}	η / μPa·s	p / MPa	ρ / mol·dm^{-3}	η / μPa·s	p / MPa	ρ / mol·dm^{-3}	η / μPa·s
					T = 298.15 K						
35.027	11.834	28.931	17.010	6.6254	22.114	4.7499	1.9241	18.578	1.3001	0.52560	17.957
33.949	11.580	28.515	16.001	6.2681	21.756	4.4998	1.8229	18.513	1.2001	0.48509	17.947
33.004	11.353	28.143	15.006	5.9093	21.424	4.2505	1.7219	18.459	1.1002	0.44468	17.935
31.995	11.105	27.743	14.004	5.5416	21.097	4.0010	1.6208	18.409	1.0002	0.40416	17.916
31.009	10.856	27.346	13.004	5.1689	20.790	3.7507	1.5193	18.355	0.90012	0.36368	17.897
30.010	10.598	26.946	12.002	4.7898	20.465	3.5007	1.4180	18.314	0.80014	0.32324	17.886
29.013	10.334	26.573	11.005	4.4075	20.179	3.2503	1.3164	18.254	0.70010	0.28277	17.871
28.009	10.062	26.199	10.001	4.0181	19.882	3.0009	1.2152	18.217	0.60012	0.24235	17.857
27.010	9.7842	25.805	9.4994	3.8217	19.735	2.7504	1.1136	18.184	0.50012	0.20193	17.849
26.005	9.4983	25.411	8.9993	3.6250	19.611	2.5003	1.0122	18.146	0.45005	0.18170	17.843
25.014	9.2099	25.030	8.5009	3.4281	19.471	2.2500	0.91063	18.098	0.40003	0.16149	17.839
24.003	8.9082	24.658	8.0009	3.2297	19.341	2.0004	0.80943	18.060	0.35005	0.14130	17.836
23.008	8.6044	24.293	7.5016	3.0308	19.212	1.8999	0.76867	18.045	0.30005	0.12111	17.824
22.001	8.2899	23.913	7.0025	2.8313	19.087	1.8001	0.72819	18.032	0.25001	0.10090	17.815
21.000	7.9701	23.535	6.5004	2.6299	18.968	1.7000	0.68763	18.015	0.20001	0.080715	17.806
20.005	7.6452	23.184	6.0054	2.4309	18.844	1.5999	0.64705	18.002	0.14999	0.060521	17.794
19.006	7.3118	22.837	5.5009	2.2275	18.719	1.5001	0.60660	17.978	0.10000	0.040348	17.778[a]
18.008	6.9720	22.468	5.0005	2.0254	18.608	1.4001	0.56612	17.969			
					T = 323.15 K						
35.066	10.892	28.525	22.011	7.5514	24.172	9.5004	3.4821	20.620	3.5026	1.3014	19.400
34.009	10.654	28.135	21.010	7.2565	23.832	9.0061	3.3063	20.500	3.0008	1.1156	19.321
33.007	10.424	27.813	19.999	6.9531	23.538	8.5042	3.1269	20.380	2.5009	0.93012	19.235
31.997	10.187	27.464	19.007	6.6497	23.229	8.0031	2.9470	20.272	2.0007	0.74436	19.168
31.013	9.9506	27.143	18.000	6.3362	22.918	7.5027	2.7665	20.153	1.5007	0.55845	19.097
30.014	9.7060	26.774	17.007	6.0214	22.616	7.0093	2.5879	20.052	1.0006	0.37239	19.031
29.014	9.4558	26.464	16.009	5.6998	22.334	6.5036	2.4041	19.935	0.80028	0.29786	19.004
28.012	9.1999	26.128	15.005	5.3710	22.050	6.0036	2.2217	19.826	0.60011	0.22336	18.983
27.000	8.9361	25.785	14.005	5.0383	21.763	5.5039	2.0388	19.756	0.40013	0.14893	18.961
26.011	8.6726	25.472	13.005	4.7006	21.510	5.0022	1.8546	19.648	0.30009	0.11169	18.946
25.005	8.3992	25.113	12.006	4.3586	21.243	4.5004	1.6699	19.570	0.20006	0.074461	18.934
24.004	8.1214	24.806	11.007	4.0124	20.977	4.0018	1.4860	19.477	0.10004	0.037236	18.904[a]
23.013	7.8409	24.510	10.007	3.6615	20.730						
					T = 348.15 K						
34.919	10.063	28.332	22.011	6.9470	24.577	9.4989	3.2036	21.503	3.5042	1.2036	20.439
34.013	9.8677	28.075	21.004	6.6718	24.308	9.0040	3.0424	21.392	3.0026	1.0324	20.367
33.000	9.6457	27.762	20.006	6.3944	24.037	8.5018	2.8780	21.292	2.5020	0.86112	20.298
32.013	9.4251	27.466	19.008	6.1121	23.781	8.0021	2.7137	21.196	2.0016	0.68953	20.228
31.015	9.1981	27.170	18.004	5.8236	23.508	7.5025	2.5486	21.099	1.5019	0.51782	20.167
30.021	8.9675	26.872	17.002	5.5313	23.255	7.0023	2.3826	21.008	1.0009	0.34535	20.111
29.000	8.7262	26.546	16.001	5.2343	22.993	6.5013	2.2156	20.918	0.80057	0.27629	20.087
27.995	8.4841	26.283	15.011	4.9366	22.742	6.0034	2.0489	20.836	0.60046	0.20729	20.073
27.005	8.2414	25.983	14.001	4.6281	22.498	5.5028	1.8808	20.742	0.40019	0.13818	20.051
26.007	7.9919	25.709	13.006	4.3201	22.267	5.0022	1.7120	20.659	0.30013	0.10365	20.041
25.007	7.7373	25.431	12.007	4.0070	22.034	4.5082	1.5449	20.583	0.20008	0.069102	20.029
24.004	7.4775	25.145	11.007	3.6893	21.817	3.9996	1.3722	20.509	0.10007	0.034566	20.005[a]
23.006	7.2140	24.864	10.001	3.3661	21.608						
					T = 373.15 K						
34.834	9.3680	28.444	22.011	6.4433	25.098	9.4991	2.9710	22.383	3.5033	1.1195	21.436
34.006	9.1977	28.207	21.015	6.1892	24.868	9.0021	2.8214	22.279	3.0035	0.96111	21.372
33.011	8.9900	27.920	19.977	5.9200	24.617	8.5043	2.6707	22.199	2.5014	0.80154	21.310
32.010	8.7772	27.653	19.005	5.6641	24.400	8.0027	2.5182	22.112	2.0021	0.64237	21.253
31.001	8.5591	27.411	18.001	5.3960	24.142	7.5007	2.3648	22.026	1.5012	0.48227	21.203
30.003	8.3396	27.138	17.018	5.1293	23.920	7.0069	2.2133	21.944	1.0005	0.32177	21.138
29.005	8.1164	26.884	16.013	4.8530	23.701	6.5074	2.0592	21.877	0.80056	0.25759	21.120
28.017	7.8916	26.616	15.013	4.5742	23.480	6.0006	1.9023	21.797	0.60066	0.19336	21.104
27.007	7.6581	26.345	14.010	4.2908	23.270	5.5047	1.7480	21.718	0.40017	0.12887	21.087
26.006	7.4225	26.099	13.002	4.0020	23.068	5.0074	1.5927	21.636	0.30098	0.096950	21.080
25.012	7.1848	25.838	12.000	3.7114	22.845	4.5016	1.4341	21.570	0.20008	0.064462	21.061
24.005	6.9399	25.586	11.006	3.4195	22.670	4.0100	1.2795	21.503	0.10025	0.032307	21.025[a]
23.004	6.6925	25.364	10.010	3.1238	22.468						
					T = 398.15 K						
35.040	8.8258	28.724	22.011	6.0157	25.676	9.5069	2.7748	23.244	3.5018	1.0466	22.418
34.043	8.6301	28.452	21.009	5.7758	25.461	9.0103	2.6357	23.173	3.0007	0.89832	22.359
33.034	8.4292	28.221	20.019	5.5352	25.246	8.5010	2.4922	23.106	2.4958	0.74839	22.305
32.013	8.2225	27.956	19.003	5.2846	25.033	8.0076	2.3524	23.020	2.0013	0.60103	22.252
31.023	8.0190	27.729	18.010	5.0365	24.822	7.5071	2.2100	22.944	1.5018	0.45171	22.204
29.911	7.7866	27.472	17.010	4.7831	24.631	7.0053	2.0665	22.871	1.0010	0.30153	22.153
29.028	7.5992	27.279	16.005	4.5250	24.434	6.5018	1.9218	22.796	0.80046	0.24126	22.131
28.028	7.3836	27.028	15.013	4.2665	24.225	6.0049	1.7784	22.734	0.60027	0.18103	22.124
27.031	7.1655	26.793	13.997	3.9988	24.047	5.5026	1.6327	22.661	0.40045	0.12083	22.102
25.977	6.9313	26.566	13.002	3.7332	23.864	5.0037	1.4875	22.601	0.30079	0.090788	22.087
25.001	6.7111	26.336	11.989	3.4594	23.685	4.5031	1.3411	22.537	0.20088	0.060649	22.072
23.993	6.4801	26.102	11.003	3.1897	23.502	4.0028	1.1942	22.474	0.10008	0.030225	22.033[a]
23.034	6.2570	25.896	10.005	2.9137	23.337						

Table 1 (Continued)

p/MPa	ρ/mol·dm^{-3}	η/μPa·s	p/MPa	ρ/mol·dm^{-3}	η/μPa·s	p/MPa	ρ/mol·dm^{-3}	η/μPa·s	p/MPa	ρ/mol·dm^{-3}	η/μPa·s
T = 423.15 K											
35.050	8.3185	29.033	22.009	5.6469	26.302	9.5043	2.6026	24.122	3.5058	0.98438	23.367
34.020	8.1254	28.815	20.987	5.4160	26.092	9.0042	2.4712	24.052	3.0023	0.84459	23.322
32.989	7.9290	28.585	20.008	5.1918	25.913	8.5030	2.3389	23.978	2.4980	0.70402	23.271
31.988	7.7356	28.366	19.008	4.9598	25.726	8.0042	2.2066	23.914	1.9978	0.56405	23.223
31.001	7.5421	28.155	17.999	4.7224	25.539	7.4979	2.0716	23.842	1.5025	0.42494	23.177
30.011	7.3450	27.942	17.009	4.4864	25.354	7.0030	1.9390	23.775	1.0011	0.28362	23.132
29.015	7.1441	27.736	16.009	4.2451	25.174	6.5023	1.8041	23.720	0.80032	0.22688	23.117
28.010	6.9384	27.529	15.002	3.9991	25.005	6.0022	1.6688	23.651	0.60023	0.17027	23.104
27.035	6.7360	27.323	14.011	3.7539	24.832	5.5028	1.5331	23.583	0.40013	0.11358	23.089
26.017	6.5215	27.107	13.002	3.5014	24.665	5.0027	1.3966	23.532	0.30044	0.085312	23.069
25.024	6.3095	26.911	11.994	3.2458	24.506	4.5012	1.2591	23.477	0.20007	0.056830	23.054
24.019	6.0917	26.691	11.004	2.9923	24.344	4.0040	1.1221	23.417	0.10005	0.028427	23.018[a]
23.014	5.8707	26.505	10.006	2.7337	24.185						

[a] Influenced by slip.

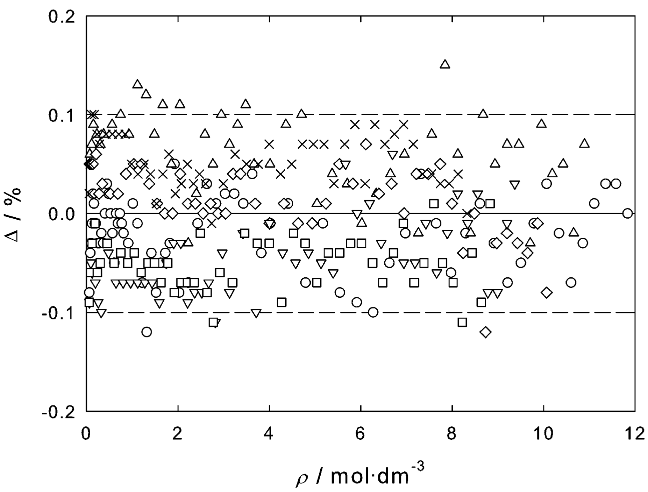

Figure 2. Evaluation of all isotherms with a double polynomial series expansion of the fourth order in the reduced density (δ) and of the second order in the reciprocal reduced temperature (τ) (eq 2). Deviations [$\Delta = 100(\eta_{exp} - \eta_{cor})/\eta_{cor}$] as a function of molar density (ρ). ○, 298.15 K; △, 323.15 K; ◇, 348.15 K; ▽, 373.15 K; □, 398.15 K; ×, 423.15 K.

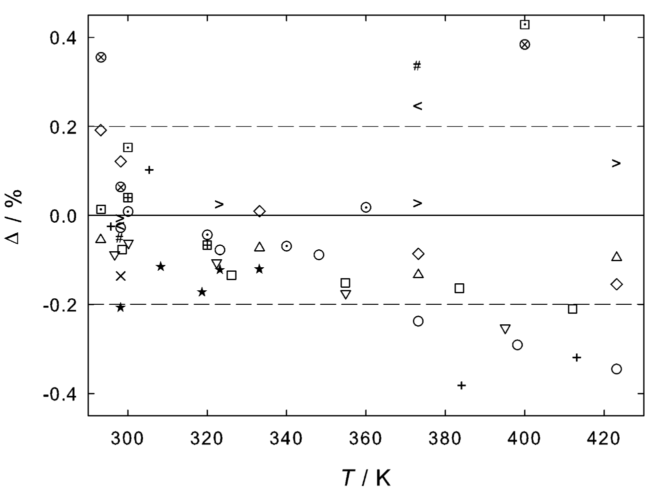

Figure 3. Comparison of reliable experimental low-density viscosity data with the correlation of Lemmon and Jacobsen.[4] Deviations [$\Delta = 100(\eta_{exp} - \eta_{cor})/\eta_{cor}$] as a function of temperature (T). Experimental data: ⊙, Clarke and Smith;[15] ⊡, Dawe and Smith;[16] ⊞, Gough et al.;[17] ⊗, Matthews et al.;[18] ★, Hoogland et al.;[19] #, Kestin et al.;[20] <, Kestin et al.;[21] >, Kestin et al.;[22] +, Timrot et al.;[23] ▽, Vogel;[24] □, Vogel et al.;[25] ◇, Docter et al.;[26,27] △, Evers et al.;[28] ×, Hurly et al.;[29] ○, present work.

is a further evidence of the high reproducibility of the present measurements.

Comparison with Literature

Several complete viscosity surface correlations are available for nitrogen (e.g., those by Stephan et al.[2] and by Millat and Vesovic[3] as well as the most recent one by Lemmon and Jacobsen[4]). As already discussed in the Introduction, the correlation of Lemmon and Jacobsen has been chosen as basis for a comparison between the present data and those of the literature.

Figure 3 illustrates for the dilute-gas region the deviations of reliable literature data as well as of the present data from the correlation by Lemmon and Jacobsen. The measurements were performed with five different techniques. Smith and co-workers[15−18] used capillary viscometers for relative measurements, whereas Hoogland et al.[19] applied an absolute one. Kestin et al.,[20−22] Timrot et al.,[23] and Vogel and his collaborators[24,25] used oscillating-disk viscometers in a relative manner. Docter et al.[26,27] and Evers et al.[28] developed a newly designed rotating-cylinder viscometer combined with a densimeter for absolute measurements. Hurly et al.[29] performed their measurements with a relative Greenspan acoustic viscometer. Figure 3 shows that all these data, including those of the present paper, agree with the correlation of Lemmon and Jacobsen at atmospheric or lower pressures within ± 0.4 %. The experimental data of Kestin et al.,[20,21,22] determined at temperatures higher than room temperature, show systematic positive deviations from the other data. This is in agreement with findings for noble gases and is probably due to a temperature measurement error in the experimental equipment of Kestin and co-workers extensively discussed by Vogel et al.[30] Furthermore, it is to consider that Smith and co-workers[15−18] directed their measurements to the ranges of very high and low temperatures connected with uncertainties of about ± 0.5 % at the temperatures under discussion. Hence, it can be concluded that the most reliable data[19,23−25,28] including those of the present paper even agree within ± (0.1 to 0.2) % between room temperature and 420 K. The difference between the basis correlation of Lemmon and Jacobsen and the most reliable data is probably caused by that Lemmon and Jacobsen do not critically evaluate the uncertainties of the measured data, which are included in the development of their correlation.

In Figure 4, the experimental data of the present paper are compared with the correlation of Lemmon and Jacobsen[4] for all six isotherms in the complete density range up to a maximum of 11.8 mol·dm^{-3}. Systematic deviations between the correlation by Lemmon and Jacobsen and the present data become evident in the limit of zero density as already shown in Figure 3.

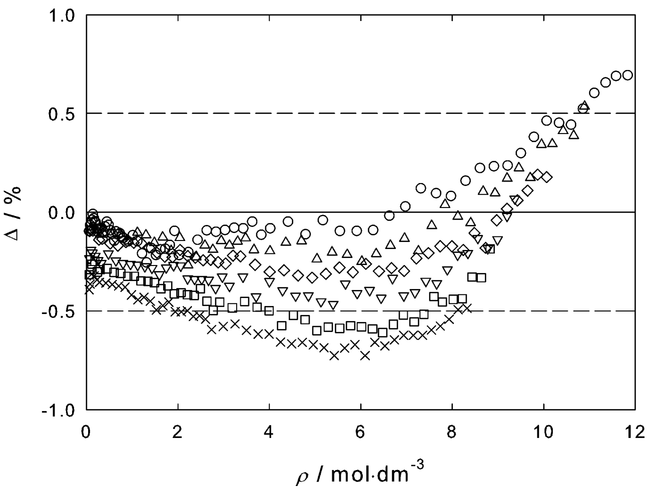

Figure 4. Comparison of the experimental viscosity data of the present paper at different temperatures with the viscosity surface correlation of Lemmon and Jacobsen.[4] Deviations [$\Delta = 100(\eta_{exp} - \eta_{cor})/\eta_{cor}$] as a function of molar density (ρ). ○, 298.15 K; △, 323.15 K; ◇, 348.15 K; ▽, 373.15 K; □, 398.15 K; ×, 423.15 K.

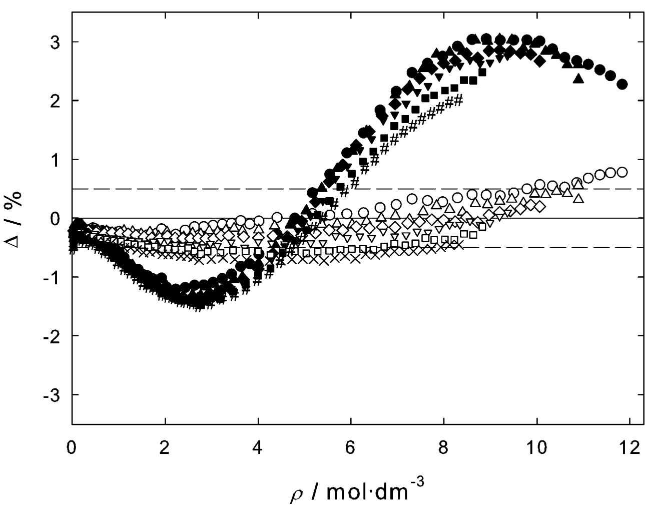

Figure 5. Comparison of the experimental viscosity data of the present paper at different temperatures with the viscosity surface correlations of Stephan et al.[2] (open symbols) and of Millat and Vesovic[3] (filled symbols). Deviations [$\Delta = 100(\eta_{exp} - \eta_{cor})/\eta_{cor}$] as a function of molar density (ρ). ○, ●, 298.15 K; △, ▲, 323.15 K; ◇, ◆, 348.15 K; ▽, ▼, 373.15 K; □, ■, 398.15 K; ×, #, 423.15 K.

Furthermore, Figure 4 reveals at moderate densities a slight difference in the initial density dependence of the viscosity. Taking into account these findings, the density dependence of the new experimental data agrees nearly perfectly with that of the correlation of Lemmon and Jacobsen up to densities of about 8 mol·dm^{-3}. But at higher densities, it is obvious that the density dependence of the viscosity differs somewhat systematically. To investigate this in more detail, the new experimental values have also been compared with directly measured data used for the development of the surface correlation of Lemmon and Jacobsen (see below). All in all, the new data show only deviations of ± 0.7 % from the correlated values in the temperature and density ranges of the measurements.

The comparison of the new experimental data with the other correlations illustrated in Figure 5 makes clear that the representation of the viscosity surface of nitrogen by Stephan et al.[2] essentially corresponds to that by Lemmon and Jacobsen. On the contrary, the correlation of Millat and Vesovic[3] disagrees completely with the other ones. The reason for that cannot be detected, because the publication of Millat and Vesovic does not provide detailed information about their calculations.

The comparison with the directly measured data from the literature is somewhat complicated since the evaluation of the measurements requires the density of the fluid and consequently an equation of state that was not the same in different papers. In addition, the viscosity data were sometimes reported as a function of temperature and pressure, but not of density. In the case that the densities were given by the authors, we used them immediately. Alternatively, we calculated ourselves the densities applying the equation of state by Span et al.[1] The experimental values of the present paper correlated with the double polynomial in density and temperature discussed in the preceding section are used for the comparison. First, we will discuss data restricted to densities up to about 6 mol·dm^{-3}.

Figure 6 shows the deviations from the experimental data of Kestin et al.,[14,31,32] all measured with oscillating-disk viscometers. Kestin and Leidenfrost[14] performed absolute measurements according to the theory of Newell.[33] Here, some data at the highest densities could already be affected by that the validity range of the measuring theory has been exceeded. The relative measurements of Kestin et al.[32] may be characterized at higher densities by larger uncertainties too. The reason is that the data of Kestin and Leidenfrost[14] were used for calibration and that the calibration curve was extrapolated to higher densities according to an inappropriate theory.[34−36] Furthermore, the relative measurements of Kestin and Leidenfrost[31] were based on older data for calibration in a large density range. Considering that our vibrating-wire viscometer has been calibrated with viscosity values of Kestin and Leidenfrost[14] in the density range up to 1 mol·dm^{-3}, it is to be noticed that the deviations enlarge systematically with increasing densities. Nevertheless, the deviations are generally within ± 0.4 % up to a density of 6.3 mol·dm^{-3} apart from one outlier.

The relative measurements of Timrot et al.[23] at temperatures between (295 and 389) K already discussed for the low-density region were also performed to densities up to nearly 5 mol·dm^{-3}. It is remarkable that, despite a slightly inferior reproducibility, the deviations between these data and the new experimental values are within ± 0.4 % up to a density of 3 mol·dm^{-3} as shown in Figure 7. Only two data are characterized by larger differences. In addition, this figure demonstrates that the results of Hoogland et al.,[19] derived from absolute measurements with their capillary viscometer in the temperature range (298 to 333) K at densities up to 5 mol·dm^{-3}, do not deviate from the present data by more than ± 0.4 %. Furthermore, Figure 7 illustrates that the relative measurements with an acoustic Greenspan viscometer by Hurly et al.[29] at room temperature and at moderate densities up to 1.3 mol·dm^{-3} resulted in values that are approximately 0.2 % lower than the present data.

Michels and Gibson[37] obtained reliable results with a capillary viscometer considering that these absolute measurements between (298 and 348) K at densities up to 20 mol·dm^{-3} were already performed in 1932. The differences between the data of Michels and Gibson and the present values do not exceed ± 0.4 up to 6 mol·dm^{-3} as shown in Figure 8. The deviations increase up to −1.5 % at higher densities up to 12 mol·dm^{-3} adherent with a larger scattering of the data of Michels and Gibson.

Figure 9 presents the results of the comparison with the data of Flynn et al.[38] and Gracki et al.,[39] both measured with an absolute capillary viscometer. The values of the present paper agree with the data of Flynn et al. within ± 0.4 %, which means up to densities of about 6.8 mol·dm^{-3}. The data of the 298 K

Table 2. Coefficients of Equation 1

T / K	n	ρ_{max} / mol·dm^{-3}	η_0 / μPa·s	η_1 / μPa·s	η_2 / μPa·s	η_3 / μPa·s	η_4 / μPa·s	σ (weighted)
298.15	4	11.83	17.788 ± 0.002	3.150 ± 0.042	8.624 ± 0.198	−4.171 ± 0.317	2.474 ± 0.160	0.037
323.15	4	10.90	18.914 ± 0.004	3.264 ± 0.067	7.662 ± 0.322	−2.652 ± 0.538	1.781 ± 0.287	0.041
348.15	4	10.06	20.010 ± 0.003	3.095 ± 0.050	8.046 ± 0.258	−3.155 ± 0.464	2.021 ± 0.267	0.027
373.15	3	9.37	21.041 ± 0.003	3.351 ± 0.042	6.233 ± 0.129	0.328 ± 0.107		0.039
398.15	3	8.83	22.060 ± 0.003	3.234 ± 0.037	6.311 ± 0.120	0.311 ± 0.106		0.031
423.15	2	8.32	23.049 ± 0.002	3.049 ± 0.012	6.715 ± 0.017			0.020

Table 3. Coefficients of Equation 2

i	η_{i0} / μPa·s	η_{i1} / μPa·s	η_{i2} / μPa·s	σ (weighed)
0	46.518 ± 0.075	−104.68 ± 0.418	86.983 ± 0.573	
1	0 ± 0	16.471 ± 0.283	−21.257 ± 0.887	
2	9.922 ± 0.305	−21.603 ± 1.748	43.360 ± 3.536	
3	0 ± 0	0 ± 0	−22.240 ± 2.175	
4	0 ± 0	55.481 ± 0.460	0 ± 0	0.057

isotherm of Gracki et al. measured up to densities of 9.4 mol·dm^{-3} are systematically lower by approximately 0.4 %.

Evers et al.[28] carried out absolute measurements with their rotating-cylinder viscometer at densities up to 10.7 mol·dm^{-3} in a large temperature range between (233 and 523) K. The comparison of the data by Evers et al. with the present values in the overlapping temperature ranges is illustrated in Figure 10. The deviations exceed ± 0.4 % only distinctly for the highest density at 293 K and at the highest common temperature of 423 K for the complete density range. The disagreement at 423 K needs further investigation in both laboratories.

Conclusions

The viscosity measurements of the present paper performed on nitrogen with a vibrating-wire viscometer are generally characterized by a reproducibility of ± 0.05 % and an uncertainty of ± (0.2 to 0.3) %. The experimental values of the six isotherms were separately evaluated in terms of the reduced density using a polynomial series expansion with a maximum power of fourth order. In addition for the purpose of comparison, the values of all isotherms together were fitted with a double polynomial series expansion in terms of the reduced density and of the reciprocal reduced temperature.

The comparison with the most recent correlation of Lemmon and Jacobsen[4] makes evident that the uncertainties estimated for this correlation are too large and can be further improved. This needs a critical judgment of the techniques and the associated theories applied for the measurements as well as a mutual comparison of the high-quality data. Thus the most reliable data[19,23−25,28] including those of the present paper demonstrate that an improved correlation could be characterized in the dilute-gas region by uncertainties of ± (0.1 to 0.2) % between room temperature and 420 K, possibly even up to 650 K. The comparison with experimental data, measured by Kestin et al.,[14,31,32] Timrot et al.,[23] Hoogland et al.,[19] Hurly et al.,[29] Flynn et al.,[38] Gracki et al.,[39] and Evers et al.,[28] and the critical

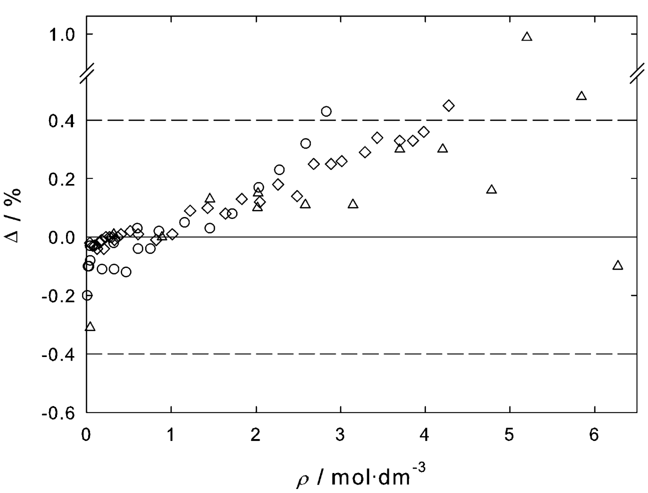

Figure 6. Comparison of experimental viscosity data from the literature with the results of the present paper at higher densitites. Deviations [$\Delta = 100(\eta_{exp} - \eta_{present})/\eta_{present}$] as a function of molar density (ρ). Experimental data: ○, Kestin and Leidenfrost,[14] (293−298) K; △, Kestin and Leidenfrost,[31] (293−296) K; ◇, Kestin et al.,[32] 298 K.

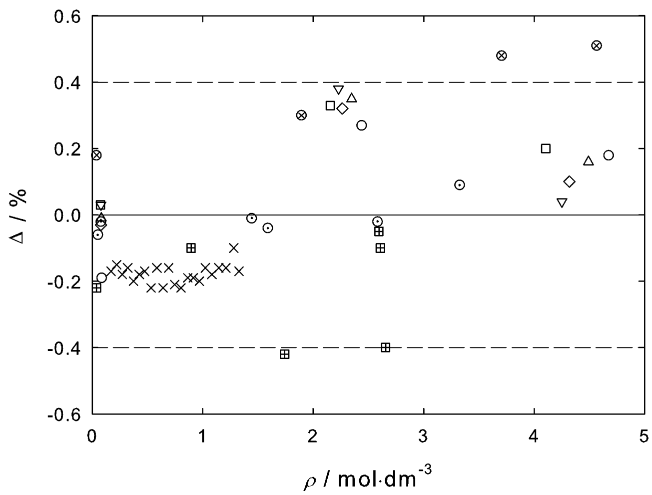

Figure 7. Comparison of experimental viscosity data from the literature with the results of the present paper at higher densitites. Deviations [$\Delta = 100(\eta_{exp} - \eta_{present})/\eta_{present}$] as a function of molar density (ρ). Experimental data: ⊙, Timrot et al.,[23] (295−298) K; ⊗, Timrot et al.,[23] 305 K; ⊞, Timrot et al.,[23] (384−389) K; ○, Hoogland et al.,[19] 298 K; △, Hoogland et al.,[19] 308 K; ◇, Hoogland et al.,[19] 318 K; ▽, Hoogland et al.,[19] 323 K; □, Hoogland et al.,[19] 333 K; ×, Hurly et al.,[29] 298 K.

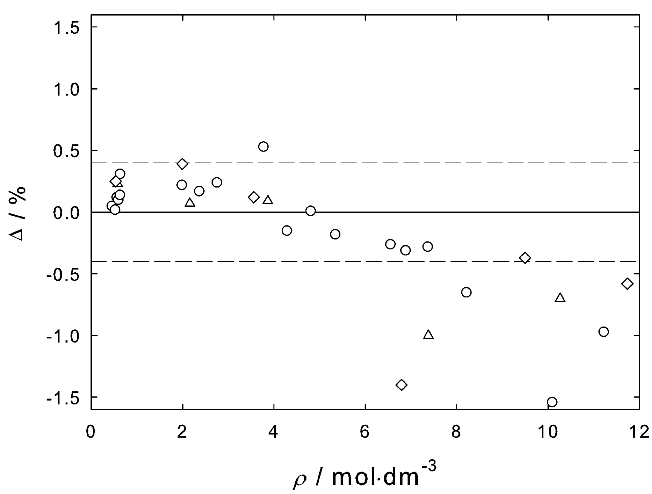

Figure 8. Comparison of the experimental viscosity data of Michels and Gibson[37] with the results of the present paper at higher densities. Deviations [$\Delta = 100(\eta_{exp} - \eta_{present})/\eta_{present}$] as a function of molar density (ρ). Experimental data: ○, 298 K; △, 323 K; ◇, 348 K.

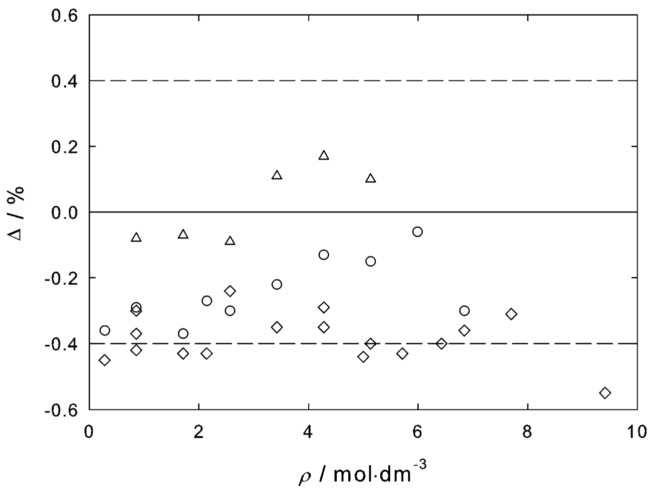

Figure 9. Comparison of experimental viscosity data from the literature with the results of the present paper at higher densitites. Deviations [$\Delta = 100(\eta_{exp} - \eta_{present})/\eta_{present}$] as a function of molar density (ρ). Experimental data: ○, Flynn et al.,[38] 298 K; △, Flynn et al.,[38] 373 K; ◇, Gracki et al.,[39] 298 K.

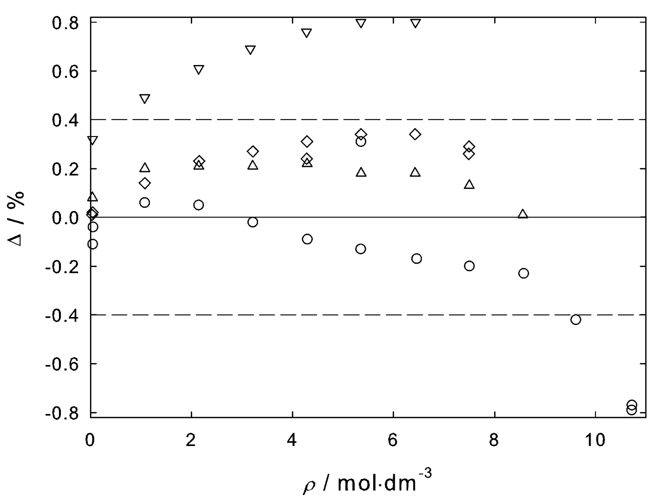

Figure 10. Comparison of the experimental viscosity data of Evers et al.[28] with the results of the present paper at higher densitites. Deviations [$\Delta = 100(\eta_{exp} - \eta_{present})/\eta_{present}$] as a function of molar density (ρ). Experimental data: ○, 293 K; △, 333 K; ◇, 373 K; ▽, 423 K.

discussion of the corresponding experiments lead to the conclusion that the uncertainties of a correlation based on these data could be decreased to ± 0.4 % in the density range up to about 10 mol·dm^{-3} between ambient temperature and 400 K. Considering the differences to the results of the present work and the data by Evers et al., there is a need for further research at high densities and at temperatures above 400 K.

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Received for review September 30, 2005. Accepted December 3, 2005.

JE050399C